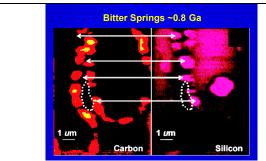
"NANO" SCALE BIOSIGNATURES AND THE SEARCH FOR EXTRATERRESTRIAL LIFE. D. Z. Oehler<sup>1</sup>, F. Robert<sup>2</sup>, A. Meibom<sup>2</sup>, S. Mostefaoui<sup>2</sup>, M. Selo<sup>2</sup>, M.R. Walter<sup>3</sup>, K. Sugitani<sup>4</sup>, A. Allwood<sup>5</sup>, K. Mimura<sup>4</sup>, and E.K. Gibson<sup>1</sup>. <sup>1</sup>NASA-JSC, Houston, TX, <u>doehler@ems.jsc.nasa.gov</u>; <sup>2</sup>LEME, CNRS Paris, France, <u>robert@mnhn.fr</u>; <sup>3</sup>Australian Centre for Astrobiology, Sydney; <sup>4</sup>Nagoya Univ., Japan; <sup>5</sup>JPL, Pasadena, CA.

Introduction: A critical step in the search for remnants of potential life forms on other planets lies in our ability to recognize indigenous fragments of ancient microbes preserved in some of earth's oldest rocks. To this end, we are building a database of nano-scale chemical and morphological characteristics of some of earth's oldest organic microfossils. We are primarily using the new technology of NanoSIMS which provides in-situ, nano-scale elemental analysis of trace quantities of organic residues. The initial step was to characterize element composition of well-preserved, organic microfossils from the late Proterozoic (0.8 Ga) Bitter Springs Formation of Australia. Results from that work [1] provide morphologic detail (e.g., Fig. 1) and nitrogen/carbon ratios that appear to reflect the wellestablished biological origin of these 0.8 Ga fossils.



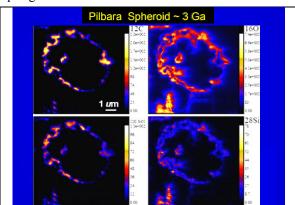
**Fig. 1.** NanoSIMS C and Si maps of Bitter Springs spheroid. Arrows tie locations on each map and illustrate silicon interspersed around carbon globules.

Nevertheless, identification of remnants of earliest life is challenging, as organic material in older, early Archean rocks tends to be poorly preserved and may include biogenic and non-biogenic components, as well as post-depositional contaminants mixed with indigenous remains. NanoSIMS can address these complexities and offers detail that could be used to interpret fragments of organic materials in poorly preserved samples were potential cellular morphology may not be intact. Thus, it seems like an ideal technique to combine with more traditional methods in efforts to characterize earth's earliest life forms.

Here we report NanoSIMS of carbonaceous materials in  $\sim 3$  and 3.43 Ga cherts from the Pilbara of Australia. Some of these carbonaceous remains are among the oldest potential structural remnants of living systems on earth [2, 3].

**Methods**: NanoSIMS was used to determine carbon (C), nitrogen (measured as CN ion), sulfur (S), silicon (Si), and oxygen (O) content for Archean carbonaceous structures in the 3.43 Ga Strelley Pool Chert (SPC)

and Mt. Goldsworthy/Mt. Grant cherts of the ~3 Ga Farrel Quartzite in the Pilbara [2,3]. Structures of interest were identified in thin section by optical microscopy. Structures analyzed by NanoSIMS included small spheroids in clusters, spindle-shaped forms, and large spheroids (Figs. 2-4). Carbonaceous material in a secondary hydrothermal vein of one sample also was analyzed (Fig. 5). NanoSIMS characteristics of the Archean samples were compared with those of the biogenic microfossils in the Bitter Springs Formation.

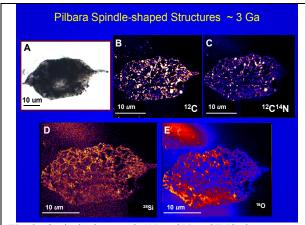


**Fig. 2.** NanoSIMS element maps of a spheroid from the Farrel Quartzite. Comparison of O and Si images (on the right) with C and CN images (on the left) illustrates Si and O interspersed around C and CN of the spheroid wall. Colors keyed to color bars for intensity.

**Results:** NanoSIMS illustrates many similarities between the Proterozoic Bitter Springs microfossils and the both the Archean spheroids and spindle-like structures (Figs. 1-4): These include the C, CN, and S distributions, CN/C ratios, the globular character and delimited, bounded style of organization of the preserved organic matter, and the occurrence of Si and O concentrations that mimic the shape of the organic remains.

Si and O in typical chert do not have a strong response in NanoSIMS, so in the Bitter Springs microfossils, the association of Si and O with C and CN (Fig. 1) was suggested to reflect a process of enhanced silica nucleation on surfaces of biological residues (which has been demonstrated experimentally) [1]. A similar relationship occurs between Si and O and C and CN in the Archean spindles and spheroids (Figs. 2, 3). This would argue that the Archean structures were present in the sample during crystallization of the silica matrix. This implies that the Archean structures cannot have been introduced to these samples after the primary

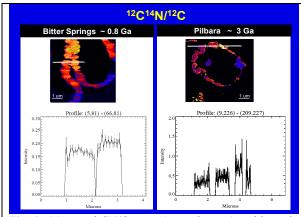
phase of silicification. The Archean structures are thus interpreted as being indigenous to the enclosing cherts. Moreover, silicification was a very early event in the history of the Archean samples, as preserved spheroids retain three-dimensional forms, suggesting that they were infilled with silica and lithified before their shapes could be flattened by compaction. It is likely, therefore, that the Pilbara spheroids and spindles are indigenous to the enclosing cherts and ~3 Ga in age.



**Fig. 3.** Optical micrograph (A) and NanoSIMS element maps (B-E) of Farrel Quartzite spindles. Colors indicate intensity.

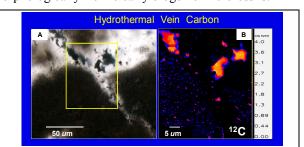
CN/C ratios of Pilbara spheroids and spindles are similar to those of Bitter Springs spheroids in that the ratios have a one-to-one correspondence with the walls and relatively uniform responses across the walls (*e.g.* Fig. 4, which shows uncorrected but similar values in Bitter Springs and Pilbara forms). This uniformity, combined with relatively high concentrations of nitrogen, is suggestive of biological origin [1].

NanoSIMS of carbonaceous material in the secondary hydrothermal vein (Fig. 5) shows a very different set of characteristics. The material in the vein is composed mainly of carbon; nitrogen content is low (CN/C is  $\sim$ 1/2 to 1/5 that of the spheroids and spindles). Si and O show no association with C and no



**Fig. 4.** Measured CN/C maps (upper images) and intensity profiles below. Lines of profile shown on upper images. Graphs have different intensity scales.

enhancement in concentration over the typical low response of Si and O in chert. This might be explained by the fact that the vein carbon was injected into the sediment after primary silicification; in addition, the vein carbon probably lacks chemical functional groups that are common in biogenic microfossils and which play a role in silica nucleation [1]. Finally, the angular, sharp-edged and dispersed (non-bounded) nature of the vein material is in contrast to the globular and bounded organization of the Bitter Springs microfossils. Thus, the carbon in the vein is distinct both chemically and morphologically from clearly biogenic microfossils.



**Fig. 5.** Carbonaceous material in a vein in the SPC. (A). Optical micrograph; yellow rectangle indicates area of (B) which is the NanoSIMS carbon map.

Discussion: The distinct character carbonaceous material in the vein provides criteria for identifying post-depositional, high temperature carbon and illustrates the potential for mixtures of differentsourced carbonaceous materials to co-exist in early Archean sediments. The disparities between this vein material and the Pilbara spheroids and spindles, coupled with the chemical and morphological similarities of the spheroids and spindles to Bitter Springs microfossils, suggests early Archean biogenicity for the spheroids and spindles. This interpretation is consistent with a growing body of data suggesting that life on Earth was well established by 3 to 3.4 Ga [4-7]. The large size and evident complexity of the spindle-like forms is noteworthy, as these structures are not simple or small, as has been assumed for earliest life. If biogenicity of the spindles is corroborated by continuing studies, their age would suggest that life on earth was not only well established by 3 Ga, but perhaps moderately advanced, These data, then, would provide new guidelines for recognizing indigenous and valid biosignatures of fragments of extraterrestrial microbes that might be encountered in meteorites or any planetary samples returned to earth in future missions.

References: [1] Oehler et al. (2006). Astrobiology 6 (6), 838-850. [2] Allwood et al. (2006). Nature 441, 714-718). [3] Sugitani et al. (2007). Prec. Res. 158, 228-262. [4] Schopf, J.W. et al. (2007). Prec.Res. 158, 141-155. [5] DeGregorio, B.T. & Sharp, T.G. (2007). GSA. Abs. Prog. 39 (6), #166-3 [6] Ventura, G.T. (2007). GSA. Abs. Prog. 39 (6), #166-4. [6] Love, G.D. (2007). GSA. Abs. Prog. 39 (6), #166-5. [7] Mojzsis, S.J. (2007). GSA Abs. Prog. 39 (6), #166-7.